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# Effects of matrix polarity and ambient aging on the morphology of sulfonated polyurethane ionomers

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## Summary

Ethylene oxide units were incorporated into the backbone of $Na^+$ sulfonated polyurethane ionomers in an attempt to induce aggregate dissociation at elevated, but observable, temperatures by reducing the incompatibility between ions and polymer. However, no dissociation could be observed by small-angle x-ray scattering (SAXS) before the onset of degradation, even when the polyol was pure EO. At 100°C and above, the SAXS patterns for all samples were quite similar, indicating morphological similarity. However, after annealing for several days at room temperature, two of the specimens appeared to develop a greater degree of microdomain order as evidenced by a narrowing of the main peak at q* and the development of a shoulder at 2q*.

## Introduction

Ionomers are polymers containing a small fraction of ionic repeat units, often defined as 10 mol% or less(1,2,3). The ionic repeat units typically bear sulfonic or carboxylic acid groups neutralized with a metal cation. Because of interionic electrostatic forces, as well as the high degree of thermodynamic incompatibility between the ionic groups and the (typically nonpolar hydrocarbon) polymer matrix, these ionic groups tend to aggregate into microdomains in the bulk material. Based on the results of small-angle x-ray scattering, SAXS(4), and recent electron microscopic(5) investigations, these aggregates are thought to be roughly spherical in shape, and a few nanometers in diameter. The large electron density difference between the aggregates and the matrix yields a strong SAXS contrast. Two features which are typically observed in ionomer SAXS patterns are a peak at a momentum transfer magnitude q* ($q = (4\pi/\lambda)\sin\theta$, where $2\theta$ is the scattering angle and $\lambda$ the wavelength of the radiation) of 0.6 - 3.5 $nm^{-1}$, and a strong upturn in scattered intensity as q approaches zero. These features have long been recognized as characteristic of ionic aggregation(6). Occasionally, a shoulder on the main peak at roughly 2q* is observed, at least in selected sulfonated polyurethane ionomers(7-9) and carboxy-telechelic polydienes(10). Recent studies using the technique of anomalous SAXS (ASAXS) on a sulfonated polyurethane ionomer of similar structure to those considered here have revealed that the relative intensities of these features remain constant as the ion-polymer x-ray contrast is changed, indicating that all three arise from scattering due to ion-polymer contrast(8,11).

Because the process of ionic aggregation is presumably enthalpically favorable and entropically unfavorable, it has been suggested that at sufficiently high temperatures the ionic aggregates should dissociate(12).

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Such aggregate dissociation has never been observed, however, most likely due to the extreme incompatibility of the ionic groups and the matrix polymer; as a result, the polymer degrades at temperatures lower than that at which the dissociation would become thermodynamically favorable. For example, the SAXS peak has been observed to persist to 300°C in ethylene/methacrylic acid ionomers(6). Observing such a transition would have not only theoretical relevance, but enormous practical importance as well. Because the ionic groups act as physical crosslinks, ionomers whose glass transition temperatures are below the use temperature behave as elastomers. Though they can be made to flow at elevated temperatures by a process termed "ion hopping", where ionic groups are transported between aggregates(13), the persistence of the ionic aggregates to high temperatures leads to melt viscosities which can be orders of magnitude greater than the analogous nonionic polymers(14). From a processing standpoint, it would be highly desirable if the aggregates could be made to dissociate at processing temperatures and reform at use temperatures.

To improve ion-matrix compatibility, we chose to increase the matrix polarity by incorporating ethylene oxide (EO) units into the backbone of sulfonated polyurethane ionomers. Poly(ethylene oxide) is known to solvate and complex with certain alkali metal salts, even at room temperature(15). In earlier studies(16) of sulfonated polyurethane ionomers based on poly(tetramethylene oxide) backbones, a suggestion of the onset of aggregate dissociation was found at 200°C when the cation was $Zn^{2+}$. Also, a sulfonated polyurethane ionomer based on pure EO polyol(7) was found to exhibit only very weak SAXS, though re-examination of this material suggested that it was extensively degraded. Here we study the $Na^+$ forms of ionomers wherein the EO content of the constituent polyol varies from 0 to 100 mol%.

## Experimental

### Synthesis and Sample Preparation

The synthetic route to this type of polyurethane ionomer has been described previously(16). An alternating copolyurethane of the polyol and toluene diisocyanate is derivatized by replacing the urethane hydrogens with sodium propylsulfonate groups. N,N'-dimethylacetamide was used as solvent here, in place of N,N'-dimethylformamide. The pure PTMO polyol was a commercial product (Quaker Chemical Polymeg, Mn = 1030 g/mol by titration). The EO-containing polyols (25, 50, and 100 mol%) were experimental products (DuPont Teracol TE). The mixed-monomer polyols are prepared by a proprietary process, and the sequence distribution is uncertain; however, as they are both clear liquids of moderate viscosity at ambient temperature, any blockiness present seems insufficient to induce microphase separation. The sulfonation level in the ionomers was determined by elemental analysis (Galbraith Laboratories) for sulfur. All ionomers were transparent elastomers with a slight yellow cast; Table I summarizes their compositions. The greater-than-100% ionization level calculated for E100 is likely due to excess sultone or its hydroxylacid contaiminating the polymer, perhaps with an additional contribution from analytical error. No homopolymerization of the sultone, or grafts longer than one sultone unti, should occur under the conditions used for synthesis(17). The mnemonic sample code used throughout this paper is Exxx, where "xxx" denotes the mole percent EO in the polyol. Samples for SAXS were compression-molded into 2.54 cm dia. disks at 180°C and 95 MPa for one hour, and allowed to cool to 50°C in the mold with the ram pressure off. It was noted that the samples flowed more easily in the mold with increasing EO content, and that the resultant specimens were tackier. Both these observations would be expected if the increased EO content lessens the ion-polymer incompatibility. All specimens were stored in a desiccator over $CaSO_4$ when not being examined; the SAXS experiments were conducted under rough vacuum.

Table I. Sulfonated Polyurethane Ionomer Compositions

| Sample | Polyol Mol% EO | Polyol Mn (g/mol) | % Sulfonation |
|---|---|---|---|
| E000 | 0 | 1030 | 98 |
| E025 | 25 | 1000 | 95 |
| E050 | 50 | 1140 | 86 |
| E100 | 100 | 1000 | 111 |

## SAXS Data Acquisition

The SAXS data were acquired on an Elliot GX-21 rotating anode x-ray generator with a copper target, at 30 kV cathode potential and 45 mA emission current. The x-rays were collimated into a beam 4.2 mm x 100 μm at the sample with an Anton-Paar compact Kratky camera, and scattered x-rays were detected with a TEC 211 position-sensitive detector. Cu Kα x-rays were selected by nickel-foil filtering and detector pulse-height analysis; approximately 600k counts were collected for each sample. The samples were heated with an Anton-Paar hot stage which has been modified in-house for use with solid sheet samples. The temperature was regulated by an Anton-Paar K-HR proportional-integral controller, using Nichrome wire heating and a Pt100 temperature sensor to achieve control of ± 2 °C and a heating rate better than 5 °C/min. To prevent flow of the samples under their own weight at elevated temperatures, specimens were held between two Kapton polyimide windows, each 127 μm thick. The sharp Kapton reflection(18) at 4 $nm^{-1}$ provided a suitable internal reference for any changes in sample thickness during the experiment. The ionomer specimens were molded to thicknesses of 0.6 - 1.0 mm, so that the sample plus 0.25 mm of Kapton gave CuKα transmittances of about 1/e for maximum scattering power. The polymers exhibited little or no degradation after being held at 200 °C for one hour; however, after 1 hour at 225-230 °C, considerable discoloration of the polymer and deposition of degradation products on the inside of the camera were noted. The data were corrected for detector sensitivity and linearity, sample thickness and transmittance, and scattering from the empty beam and Kapton windows, placed on an absolute scale ($I/I_eV$, where $I_e$ is the intensity scattered by a single electron and V the scattering volume), smoothed and desmeared as described elsewhere(8,11).

## Results and Discussion

Figures 1 and 2 show the SAXS patterns for the four ionomers at temperatures ranging from 22-200 °C, collected on heating. Note that each curve above 22 °C has a progressive intensity offset to avoid overlap of the curves (factors of 2 were used for E000, E025, and E050, while factors of 2.5 were used for E100). Each specimen had been stored at ambient conditions (about 25 °C) for 13-16 days before observation. All materials exhibit a peak at q* near 1.3 $nm^{-1}$ and the usual upturn in scattered intensity as $q \rightarrow 0$. This peak persists to 200 °C for all four ionomers, indicating that the ionic aggregates do not dissociate within this temperature range. Slight shifts in peak position are evident, especially for E100, which may indicate some aggregate rearrangement; however, these shifts are too small to indicate any major structural change. Even with the highly polar PEO polyol, then, the incompatibility between the sodium sulfonate groups and the backbone remains too great to induce a homogenization of the ionic and nonionic components.

Despite the similarity of the SAXS patterns between specimens at 100 °C and above, the 22 °C patterns reveal interesting differences between the samples. In particular, the E000 and E050 materials exhibit relatively

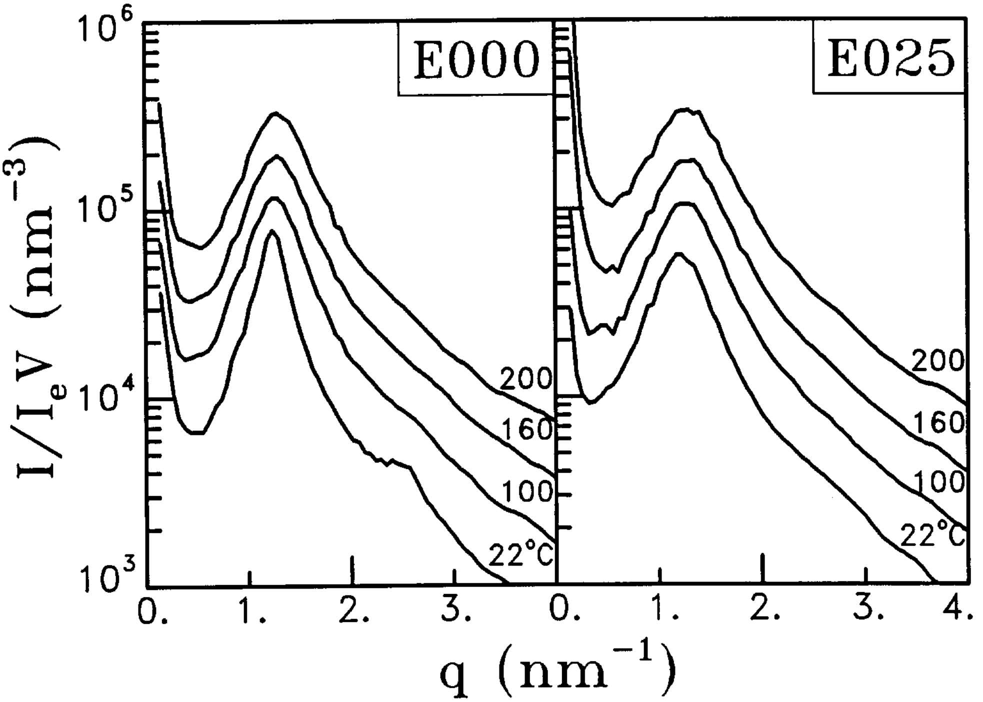

**Figure 1.** (Left): SAXS curves for E000 (annealed 13 days at ambient), and (right): E025 (annealed 14 days at ambient), at (bottom to top): 22, 100, 160, 200°C. An offset of x2 is applied successively to each curve beyond that for 22°C to improve clarity.

narrow main peaks with a shoulder near 2q*, while the E025 and E100 samples have a broad peak with no shoulder. The precise origin of the shoulder remains an unsolved question(8), but ASAXS experiments clearly show that it is related to the ionic groups(8,11), and it is reasonable to interpret the narrow peak and shoulder as evidence of a more highly ordered microdomain structure in those materials which exhibit them. Numerous sulfonated polyurethane ionomers have been synthesized in our laboratory with molecular architectures similar to the materials studied here, a few of which show this high-q shoulder(7-9). However, the molecular features which give rise to the shoulder remain unclear. For example, Ding(7) studied a material very similar to E000, except that the diisocyanate was methylene *bis*(p-phenyl isocyanate). There, the shoulder was quite intense at room temperature (within an order of magnitude of the main peak) and disappeared abruptly between 205 and 220°C, at the same point where degradation was observed in the present study. Furthermore, Ding also studied a specimen from another batch of E000, cast from solution, and did not observe the shoulder(16). Here, the intensity of the shoulder does not vary in a regular way with polyol composition, the only known variable which varies significantly between polymers. Another potential variable which may be relevant is the molecular weight of the base polyurethane, and whether it is degraded in the derivatization. Solution studies of polyurethane ionomers will be pursued in the future to address this point.

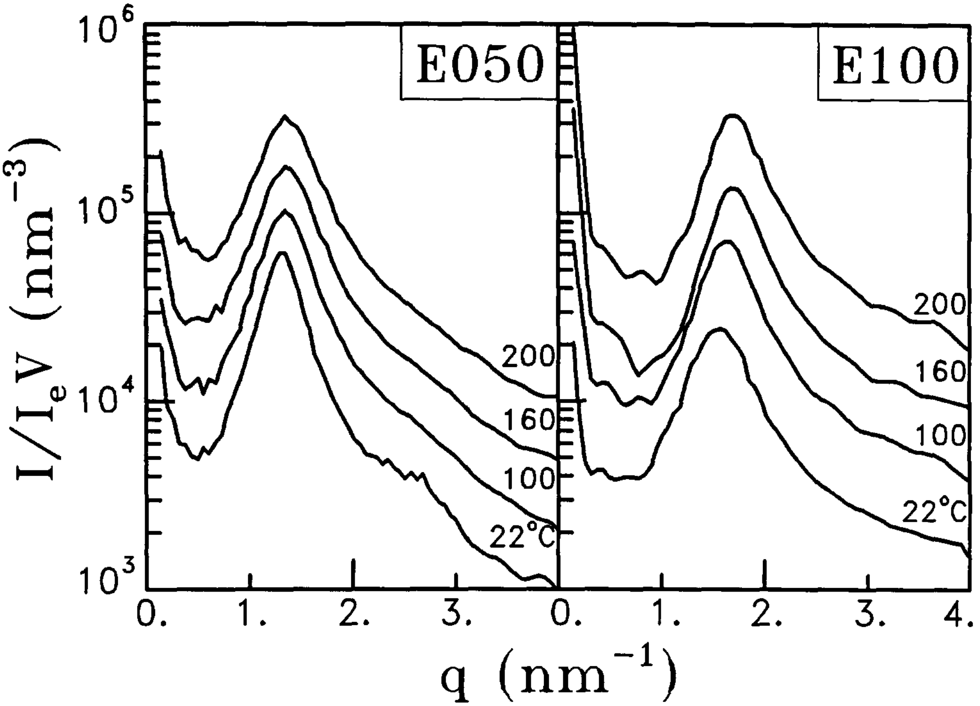

**Figure** 2. (Left): SAXS curves for E050 (annealed 15 days at ambient), and (right): E100 (annealed 16 days at ambient), at (bottom to top): 22, 100, 160, 200°C. An offset of (x2 left, x2.5 right) is applied successively to each curve beyond that for 22°C to improve clarity.

If a higher degree of microdomain order is present in E000 and E050 at room temperature, it must be quite tenuous, as heating to 100°C destroys the shoulder and broadens the main peak. In view of the high melt viscosity of these ionomers, the reverse process on cooling may be quite slow. To investigate this hypothesis, a second molding of E000 was prepared, and equilibrated with the laboratory temperature (about 25°C) for three days before measurement. The molding was then cut in half and the SAXS pattern of one half recorded to give the "3-day" pattern. The same piece was then heated to 100° in the hot stage, allowed to cool to 22°C, and its SAXS pattern recorded to give the "0-day" pattern. Both halves were examined seven days later to give "7-day" and "10-day" patterns. Finally, the original sample was reexamined 52 days after molding. All the SAXS patterns are presented in Figure 3, again with a progressive intensity offset of a factor of 2. The evolution of the SAXS pattern with room-temperature annealing is clear: the main peak narrows and the shoulder develops, with a characteristic time of order 10 days. The 13-day and 52-day patterns are not significantly different; this was found to be the case for E025, E050, and E100 as well. Since the rate of this process is expected to be quite sensitive to the temperature of annealing (as 100°C is sufficient to reverse it), the characteristic temperatures for the two moldings may not be exactly comparable, but the trend is plain. More detailed examination of Figure 3 also shows that the peak and shoulder both move to slightly lower q with annealing time, and maintain a q-ratio very close to 2.

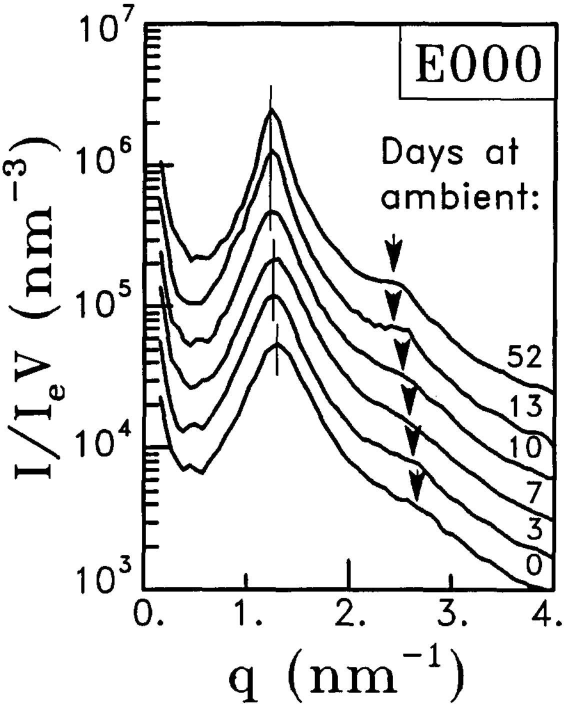

**Figure 3.** SAXS curves for E000 at (bottom to top): 0, 3, 7, 10, 13, 52 days annealing at ambient temperature. An offset of x2 is applied successively to each curve beyond that for 0 days to improve clarity. Vertical lines denote approximate position of main peak; arrows denote approximate position of shoulder.

While the SAXS evidence indicates a slow morphological change for these materials at ambient temperature, the impact of this process on material properties remains unknown. In the future, it would be interesting to follow this process by dilatometry or by modulus measurements in parallel with SAXS, which may shed additional light on its precise nature. To induce aggregate dissociation, it may prove profitable to modify the ionic group as well as the polymer backbone, such as employing carboxylate rather than sulfonate groups.

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